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Time-Domain Measurement of Spontaneous Vibrational Decay of Magnetically Trapped NH

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Abstract

The $v = 1 \rightarrow 0$ radiative lifetime of NH ($X^3\Sigma^-, v = 1, N = 0$) is determined to be $\tau_{rad,exp.} = 37.0 \pm 0.5_{stat} {}^{+2.0}_{-0.8_{sys}}$ ms, corresponding to a transition dipole moment of $|\mu_{10}| = 0.0540 {}^{+0.0009}_{-0.0018}$ D. To achieve the long observation times necessary for direct time-domain measurement, vibrationally excited NH ($X^3\Sigma^-, v = 1, N = 0$) radicals are magnetically trapped using helium buffer-gas loading. Simultaneous trapping and lifetime measurement of both the NH($v = 1, N = 0$) and NH($v = 0, N = 0$) populations allows for accurate extraction of $\tau_{rad,exp.}$. Background helium atoms are present during our measurement of $\tau_{rad,exp.}$, and the rate constant for helium atom induced collisional quenching of NH($v = 1, N = 0$) was determined to be $k_{v=1} < 3.9 \times 10^{-15}$ cm³s⁻¹. This bound on $k_{v=1}$ yields the quoted systematic uncertainty on $\tau_{rad,exp.}$. Using an *ab initio* dipole moment function and an RKR potential, we also determine a theoretical value of 36.99 ms, in agreement with our experimental value. Our results provide an independent determination of $\tau_{rad,10}$, test molecular theory, and furthermore demonstrate the efficacy of buffer-gas loading and trapping in determining metastable radiative and collisional lifetimes.

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Measurement of molecular abundances in astrophysical, atmospheric, and chemical settings is critical to the discovery of new physics. A myriad of techniques are used to accomplish this. One in particular, infrared absorption spectroscopy, studies light passing through a sample (*e.g.* an atmosphere or stellar cloud) to determine total absorption. In combination with transition strengths measured in the lab, molecular density can be determined. However, measurement of transition strengths for rovibrational transitions of radicals is particularly difficult [1]. This is generally due to imprecise knowledge of the radical density. One approach that removes the need for absolute density calibration is time domain or linewidth measurement of the transition lifetime. Despite the intrinsic advantages of this approach, it has been seldom used for weak transitions. This is because measurement of lifetimes longer than a few milliseconds is difficult; the long measurement time required can be limited by collisional quenching or transit time. A by-product of these experimental limitations has been the increasing importance of *ab initio* calculations in determining transition strengths [2].

One “striking” example of the need for improved experimental methods and verification of *ab initio* techniques is the case of imidogen (NH). The NH vibrational radiative lifetime τ_{rad} is a vital number for astrophysical studies since the $\Delta v = 1$ transitions of the $X^3\Sigma^-$ state fall in the 3 μm atmospheric transmission window. The absolute line strength of the 0-1 vibration-rotation (V-R) transition (A_{10}) plays a crucial role in determining the nitrogen abundance in cool stars [3, 4, 5, 6], which, in turn, is tied to questions of stellar evolution and internal mixing. The estimated absolute nitrogen abundance of the sun is based on atomic nitrogen (Ni) lines and NH V-R absorption [7]. The lack of precise knowledge of A_{10} is the dominant source of uncertainty in observed abundances based on V-R lines [8]. Despite their importance, measurements of the NH V-R transition strengths are particularly lacking [8, 9, 10].

Chackerian, Jr. *et al.* [11] have made the only published laboratory measurements of τ_{rad} for NH by observing the intensity variation introduced by the vibration-rotation interaction (the Herman-Wallis effect [12]) and combining this with the only measurement of the permanent electric dipole moment [13] of $\text{NH}(X^3\Sigma^-)$. This experimental determination and the published theoretical values [2, 8, 10, 14, 15] cover a range spanning nearly 50%.

In this Letter we report a direct time-domain measurement and *ab initio* theoretical calculation of the spontaneous emission lifetime of vibrationally excited $\text{NH}(v = 1, N = 0)$

radicals. NH ($v = 1$ and $v = 0$) is loaded into a magnetic trap using ^3He buffer-gas loading. The trap lifetime of NH($v = 1$) is measured to be $\tau_{\text{trap},v=1} = 33.5 \pm 0.5$ ms, dominated by the radiative lifetime ($\tau_{\text{rad},10}$). Corrections to the measured lifetime due to the finite trap evaporation (determined from our measured NH($v = 0$) lifetime) and the possibility of background helium collisional quenching ($k_{v=1}$) result in $\tau_{\text{rad},\text{exp.}} = 37.0 \pm 0.5_{\text{stat}}^{+2.0}_{-0.8\text{sys}}$ ms, in agreement with our calculated value of 36.99 ms. We also measure a tight bound on the helium-induced NH($v = 1$) collisional quenching rate coefficient of $k_{v=1} < 3.9 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$.

In 1998 our group demonstrated the first magnetic trapping of molecules [16] by buffer-gas loading CaH($v = 0$). It was discovered that both $v = 0$ and $v = 1$ states were coolable and CaH($v = 1$) persisted in the buffer gas as long as CaH($v = 0$) [17], suggesting that the collision-induced quenching of vibrational states in the buffer gas was slow enough to utilize buffer-gas loaded molecules to measure vibrational decay lifetimes. In 2005, the Meijer group in Berlin used a very different method, Stark-deceleration [18] and optical pumping, to electrostatically trap OH($v = 1$) and perform the first vibrational lifetime measurement of cold trapped molecules [19]. Their measurement improved the precision of the experimentally determined Einstein A coefficient A_{10} to better than 4% and was in agreement with their *ab initio* calculated value. Our group recently demonstrated trapping of $^3\Sigma$ state molecules with the buffer-gas loading of ground-state NH into a magnetic trap [20]. The large splitting between levels of opposite parity in molecules in Σ states makes them unsuitable for Stark deceleration due to nonlinear Stark shifts [18] but well suited for buffer-gas loading. We find that unlike CaH, the lifetime of the vibrationally excited NH molecules in the trap is significantly shorter than the ground state due to spontaneous emission.

The experimental apparatus and method is essentially the same as that described in Ref. [20]. Briefly, NH radicals are loaded into a magnetic trap from a molecular beam. About $\approx 10\%$ of the NH produced in the beam by dissociating ammonia in a DC glow discharge is in the $v = 1$ state. We do not detect any NH($v = 2$). The NH($v = 1$) along with NH($v = 0$) enter the magnetic trap, which is inside a cold buffer-gas cell. The cold cell has a 1 cm diameter entrance aperture for loading the NH radicals from the beam so that the buffer gas exits through the aperture but is replenished through a fill line. The flow rate of buffer gas into the cell is controlled to set the buffer-gas density at a constant level. Low-field seeking molecules fall into the 3.9 Tesla magnetic trap and are detected using either laser

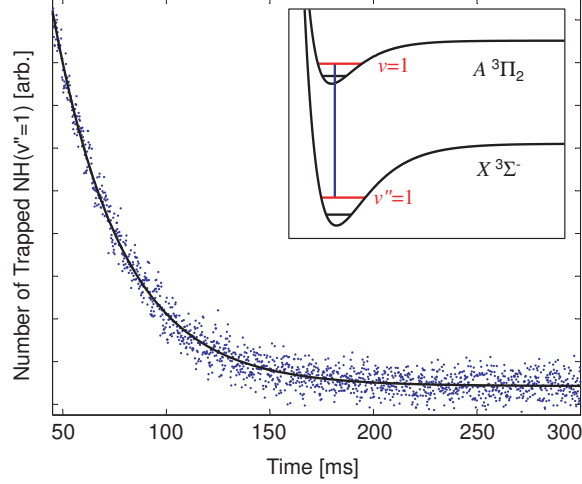


FIG. 1: Vibrationally-excited trapped molecule density vs. time. The population of the NH $X^3\Sigma^-(v'' = 1, N = 0)$ molecules is monitored using laser-induced fluorescence on the 1-1 band of the $A \leftrightarrow X$ transition (see inset), and the time profiles are fitted to a single-exponential decay to obtain observed lifetimes. The loading process that occurs in the first 50 ms is essentially the same as described in [20], and we begin fitting as least 5 ms after the molecular beam has been turned off to ensure rotational and translational thermalization.

induced fluorescence (LIF) or laser absorption on the $A \leftrightarrow X$ transition. Laser absorption spectroscopy indicates that we typically trap more than 2×10^8 NH($v = 0$) molecules. The excitation laser is a 672 nm CW dye laser frequency doubled to 336 nm [34]. Thermalization of the external and rotational motion of the NH proceeds rapidly, as can be verified from their trapped lifetime and the Zeeman-broadened spectrum [20].

NH($v = 0$) and NH($v = 1$) are detected from the rotational ground state ($N = 0$) on the diagonal vibrational lines of the R_1 $A \leftrightarrow X$ transition. Figure 1 shows a measurement of the number of trapped NH($v = 1$) versus time, *i.e.* the fluorescence observed due to our continuous excitation of the $A \leftarrow X$ transition. Lifetimes are measured by χ^2 -fitting the fluorescence to a single exponential and the measured lifetime does not depend on laser power in this range. The χ^2 fits are derived from error bars empirically determined from repeated LIF counting measurements and calculated shot noise. Figure 2 shows the measured trap lifetime of both NH($v = 1$) and NH($v = 0$) vs. buffer-gas density at a temperature of 615 mK. The vibrational ground state lifetime shows the previously studied dependence on buffer-gas density [20]. At low buffer-gas densities, the helium enhances the trap lifetime by

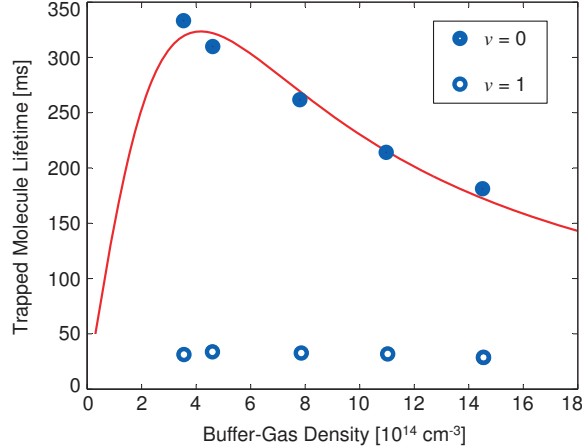


FIG. 2: Measured trap lifetime for $\text{NH}(v=0)$ (closed circles, τ_{hold}) and $\text{NH}(v=1)$ (open circles, $\tau_{\text{trap},v=1}$). For the $\text{NH}(v=0)$, the lifetime is set by a combination of the trap depth, the diffusion enhancement of the lifetime, and collision-induced Zeeman relaxation. The solid curve is a fit to the expected functional form [20]. The lifetime of $\text{NH}(v=1)$ is limited by the spontaneous emission lifetime.

enforcing diffusive motion of the trapped molecules. As the buffer-gas density is increased further, the lifetime is suppressed due to the higher frequency of Zeeman relaxation collisions with helium. In contrast, the measured lifetime of the $v=1$ state ($\tau_{\text{trap},v=1}$) shows very little buffer-gas density dependence, as is expected for spontaneous radiative decay.

Figure 3 shows trap lifetimes for $\text{NH}(v=0)$ and $\text{NH}(v=1)$ as the temperature of the buffer gas is varied. The $\text{NH}(v=0)$ data show the expected strong dependence of lifetime on trap depth, as described in Ref. [20]. In contrast, the $\text{NH}(v=1)$ trap lifetime changes by less than 5 ms over this range, which again demonstrates that the lifetime is not dominated by either trap depth or collisions. This is again consistent with spontaneous radiative decay.

The spontaneous radiative lifetime of $\text{NH}(v=1)$ is measured using the following procedure. We repeatedly measure the lifetime of trapped $\text{NH}(v=1)$ at 615 mK with buffer-gas density $n_{\text{He}} = 3.6 \times 10^{14} \text{ cm}^{-3}$. This measurement is done at the low end of our workable buffer-gas density range, resulting in relatively long lifetimes for trapped $\text{NH}(v=0)$, thereby reducing the effect of finite trap lifetime on the measured value of $\tau_{\text{rad,exp.}}$. Data is obtained from 1041 trapping cycles and fluorescence intensity time profiles taken over four hours, yielding a measured $\text{NH}(v=1)$ trap lifetime of $\tau_{\text{trap},v=1} = 33.5 \text{ ms}$ with a standard error of $\pm 0.5 \text{ ms}$.

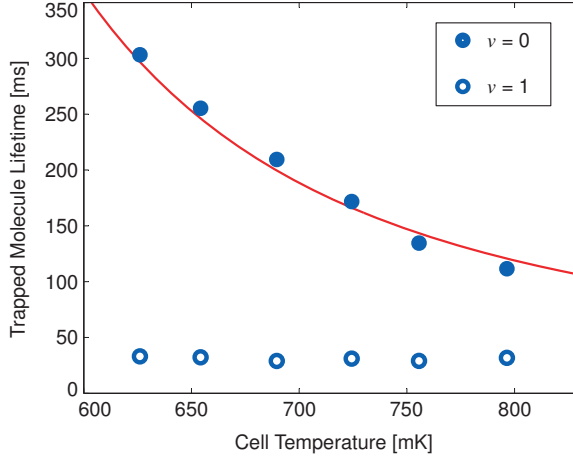


FIG. 3: Measured trap lifetimes for the ground (closed circles) and first vibrationally excited states (open circles) of NH vs. buffer-gas temperature. The $v = 0$ molecules show the previously studied strong dependence on temperature [20]. The solid curve is a fit to the expected functional form. The $v = 1$ state shows very little dependence on buffer-gas temperature.

In order to extract the $1 \rightarrow 0$ spontaneous radiative lifetime ($\tau_{rad,exp.}$) from the measured trap lifetime ($\tau_{trap,v=1}$), the finite hold time of the trap (τ_{hold}) as well as additional loss mechanisms unique to the vibrationally excited molecules (τ_{loss}) must be taken into account. $\tau_{rad,exp.}$ can be written

$$\tau_{rad,exp.} = \frac{1}{\tau_{trap,v=1}^{-1} - \tau_{hold}^{-1} - \tau_{loss}^{-1}}. \quad (1)$$

The finite trap hold time effects are measured directly by observing the trap lifetime of NH($v = 0$). Given that the magnetic moment of NH($v = 1$) is identical to NH($v = 0$), this gives a simple correction of $\Delta\tau = +3.5 \pm 0.1$ ms.

Among the possible mechanisms that would cause population changes in NH($v = 1$), background helium collision-induced loss is the only likely mechanism we can identify for our system. We will refer to this loss mechanism as vibrational quenching, although it should be noted that if the collision-induced Zeeman relaxation for the $v = 1$ state is different from the $v = 0$ state, it would manifest itself with the same functional dependence on n_{He} as direct $v = 1 \rightarrow 0$ quenching. In order to quantify this possible effect, we fit the data in Fig. 2 assuming as a free parameter helium collision-induced loss of NH($v = 1$) (after correcting $\tau_{trap,v=1}$ for the trap hold time). This attempted fit results in a collisional-quenching rate

coefficient of $1.1 \pm 2.8 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$, consistent with zero. This implies an upper limit on the collisional quenching rate coefficient for $\text{NH}(v = 1)$ of $k_{v=1} < 3.9 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$ and a consequent systematic correction of the lifetime from this possible effect of between -0.8 and $+2.0$ ms where the negative value would correspond to slower Zeeman relaxation for $v = 1$ than $v = 0$. This is the dominant systematic uncertainty in our measurement, which yields a final value of $\tau_{\text{rad,exp.}} = 37.0 \pm 0.5_{\text{stat}}^{+2.0}_{-0.8_{\text{sys}}}$ ms where the second uncertainty is the systematic uncertainty (completely due to our measured limit on the collision-induced quenching rate coefficient). Fractional corrections to the lifetime from blackbody radiation [21], hyperfine splitting [22] and Zeeman shifts [22] are calculated to be negligible ($< 10^{-4}$).

We can use this measurement to extract the dipole matrix element for this transition, $\mu_{10} \equiv \langle \phi_{v=1,N=0} | \mu | \phi_{v=0,N=1} \rangle$ where $\phi_{v,N}$ is the vibrational wavefunction. The spontaneous emission lifetime can be written in terms of the vibrational transition dipole moment as

$$\tau_{\text{rad},10} = \frac{3c^2e^2}{4\alpha\omega^3} |\langle \phi_{v=1,N=0}(r) | \mu(r) | \phi_{v=0,N=1}(r) \rangle|^{-2}, \quad (2)$$

where α is the fine-structure constant and ω is the transition frequency. The final rotational state for the decay to $v = 0$ is $N = 1$ due to the parity selection rule. We calculate the contribution to the lifetime from the $N = 3$ final state to be negligible ($< 10^{-5}$). Taking $\omega = 3092.88 \text{ cm}^{-1}$ from spectroscopic constants in the literature [23, 24] gives us a measured value of $|\mu_{10}| = 0.0540^{+0.0009}_{-0.0018} \text{ D}$.

Comparison of our experimental value of $\tau_{\text{rad,exp.}}$ to theory is crucial to claim resolution of the conflicting published measured and theoretical values. To obtain a state-of-the-art calculated value we perform an *ab initio* calculation of the spontaneous emission lifetime of $\text{NH}(v = 1)$. The vibrational wave function $\phi_{v=1,N=0}(r)$ was computed by solving the one-dimensional Schrödinger equation with the sinc-function discrete variable representation method [25]. The radial potential was constructed with the RKR method [26], using the Dunham parameters from Ram *et al.* [23, 24]. To compute $\phi_{v=0,N=1}(r)$ the centrifugal term was added to the potential. The MOLPRO program package [27] was used to compute the r -dependent electric dipole moment function $\mu(r)$. We used the internally contracted multireference single and double excitation configuration interaction (MRCI) method [28] and the aug-cc-pV6Z one electron basis. The orbitals were obtained in a complete active space self consistent field (CASSCF) calculation. The active space consisted of the $1\sigma - 6\sigma$, $1\pi - 3\pi$, and $1\delta - 2\delta$ orbitals. All CASSCF configurations were used as reference

configurations in the MRCI calculation. The result is a calculated spontaneous emission lifetime of 36.99 ms, in excellent agreement with our measured value.

To get an indication of the accuracy of the *ab initio* calculation we also computed the spectroscopic constants and the lifetime using the MRCI potential instead of the RKR potential. This results in a transition frequency that is 0.44% too high, a ground state rotational constant that is 0.48% too high and a computed lifetime of 37.29 ms.

Another indication of the accuracy of the *ab initio* calculation was obtained by computing the dipole function with the partially spin restricted coupled cluster method with single and double excitations and a perturbative treatment of the triples (RCCSD(T)) [29, 30, 31]. This is a single reference method and the orbitals were taken from a restricted Hartree Fock calculation. Core-excitations were included and the aug-cc-pV6Z basis was used. The dipole was obtained in a finite field calculation with electric fields of $\pm 10^{-4} E_h/a_0$. With the vibrational wave functions computed for the RKR potential this results in a lifetime of 37.39 ms. The transition frequency computed with the RCCSD(T) potential is 0.73% too high.

Using the MRCI dipole moment function we also computed the $\text{NH}(v=0)$ *permanent* dipole moment. The result, 1.5246 D, is 10% larger than the 1974 experimental value of 1.38 ± 0.07 D [13] but it agrees well with the 1996 *ab initio* value of 1.536 D Paldus and Li [32], who already express doubt about the experimental value.

While both our measured and calculated values for the transition dipole moment agree, they differ significantly from previously published values. Chackerian, Jr. *et al.* [11] have observed the Herman-Wallis effect and combined their spectroscopic data with the 1974 measured value of the static dipole moment of ground-state NH [13]. This results in a measured value for the transition dipole moment of $|\mu_{10}| = 0.0648 \pm 0.008$ D, which they present with a calculated *ab initio* value [11] of $|\mu_{10}| = 0.0594$ D. These transition dipole moments are inconsistent with our result of $|\mu_{10}| = 0.0540^{+0.0009}_{-0.0018}$ D. Grevesse *et al.* provide a plot of the calculated dipole moment matrix element (including rotation) vs. N'' that gives a value of $|\mu_{10}| > 0.06$ D for $N'' = 1$ [8]. Cantarella *et al.* use a series of different published potentials and dipole moment functions to calculate dipole matrix elements falling in the range of $0.0528 \leq |\mu_{10}| \leq 0.0618$ D [2]. Das *et al.* calculate and oscillator strength corresponding to $|\mu_{10}| = 0.0526$ D [15].

Our measured lifetime $\tau_{\text{rad,exp.}} = 37.0 \pm 0.5_{\text{stat}}^{+2.0}_{-0.8\text{sys}}$ ms can also be compared to published

values of the Einstein A coefficient using $A_{10}^{-1} = \tau_{rad,10}$. Rosmus and Werner [14] calculate $A_{10}^{-1} = 28.7 \pm 4$ ms, and Dodd *et al.* [10] calculate $A_{10}^{-1} = 19.3$ ms. Both of these calculations neglect rotation, and we find convergence for our calculated value only after inclusion of the large basis and active space described above. Despite these discrepancies, our measurement is in agreement with our *ab initio* calculated value and we believe this new value to be the most accurate yet reported.

In conclusion, we have measured the spontaneous emission lifetime of the $X^3\Sigma^-(v = 1, N = 0)$ state of the NH radical in a magnetic trap and performed a new *ab initio* calculation and find these in good agreement. This new value can be used to calibrate molecular densities in spectroscopic measurements on the NH $1 - 0$ transition. Since previously published values for the transition dipole matrix element are almost all larger than our measured value, it is likely that NH densities that have been inferred from V-R absorption on this line are lower than the actual density of NH radicals. We estimate that current solar nitrogen abundance estimates derived from this transition [7, 8, 33] will require a correction of about 30%.

Using buffer-gas loading at low helium densities, we have shown the effect of the buffer gas to be small enough to measure the lifetime of $\tau_{rad,10}[\text{NH}]$ in a magnetic trap with the highest precision yet reported. Since the Zeeman relaxation cross section for $v = 1$ and $v = 0$ are unlikely to be very different, future measurement of the vibrational quenching cross section of $\text{NH}(v = 1)$ with helium may reduce the systematic error bars of this measurement to less than our current statistical uncertainty. Our work demonstrates a new application for buffer-gas loading that can benefit the physics, astrophysics, and chemistry communities.

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